MULTIPLE LAYERED FUNCTIONAL THIN FILMS

FIELD OF INVENTION

The present invention relates to a functional thin film and a method of making the same, more particularly, to the preparation of a novel ultrathin film, i.e. a thin film regulated at a molecular level by the utilization of the alternate layer-by-layer method.

BACKGROUND OF THE INVENTION

Most biological reactions proceed through highly efficient and selective physical and chemical processes in which proteins such as enzymes or functional pigment molecules work singly or in a cooperative or sequential manner. In order to artificially mimic such functions for developing novel molecular devices such as enzyme reactors, biosensors or luminescent elements, it is necessary to build up a structure or assembly in which functional molecules are layered in a desired sequence. Generally, functional molecules can be layered onto a solid support by one of the following methods: (i) the LB method in which a thin film developed on the surface of a liquid is transferred onto a suppoirt, (ii) the monolayer adsorption method by which functional molecules are fixed directly on a solid support, and (iii) the alternate layer-by-layer method for fixing functional molecules through adsorption alternately with other molecular components.

The LB method is known as a method for preparing a thin film in which the molecular layers are arranged in a desired order with a precision of molecular level. The method comprises dissolving an amphiphilic substance such as a lipid in an organic solvent, spreading a monolayer on an aqueous surface and transferring the monolayer onto a solid substrate, thereby forming a thin film with a desired thickness by controlling the order of the layers. This method suffers from a restriction that it is only applicable to water-insoluble substances having properties similar to surfactants, since the subject substance must be developed on an aqueous surface as a monolayer. In addition, the LB method has a drawback in that it has a poor productibility and requires a device which is expensive and not easy to handle.

The monolayer adsorption method is to fix molecules dissolved in a solution, onto a solid support as a monolayer taking advantage of a strong interaction such as that between silanol and glass or thiol and gold. This method is advantageous in that a water-soluble substance can be employed. It has additional merits that the resultant film is resistant to external actions because of the strong interaction between the solid support and the monolayer and that the fixation can be made regardless of the shape of the solid support. However, the method has a fatal drawback in that chemical reactions with specific functional groups are indispensable for the preparation of a multi-layered structure and thus the substances usable are restricted to those having the specific functional groups which will interact with the support material.

The alternate layer-by-layer method is to prepare a thin film through alternate adsorption of oppositely-charged substances which may be selected in combination from among organic polymer ions, inorganic polymer ions, proteins and the like. The principle of this layering method is as follows: If there is immersed in a solution of polymer ions a solid support whose surface electric charge is opposite to that of the polymer ions, the polymer ions are adsorbed onto the support due to electrostatic interaction. This results in the neutralization of the surface charge of the support by the polymer ions and then the generation of new electric charge due to overadsorption of the polymer ions. Thus, if the resultant assembly is immersed in a solution of a substance having an electric charge opposite to that of polymer ions, for example, in an aqueous solution of a protein, another new electric charge is generated on the surface due to the charge neutralization and the overadsorption. Repetition of this process will enable alternate layering of such substances as polymer ions and proteins in a desired order and substantially in an indefinite manner. The extent of the overadsorption in each step is limited by the charge saturation and thus a limited amount of the polymer ions are fixed on the surface in each step. This method is advantageously carried out in a simple manner without need for any sophisticated devices. The method is also meritorious in that it is suitable for use in the fixation of easily denaturable molecules such as proteins, since a solution of such substance can be directly employed.

However, the alternate layer-by-layer method is not applicable to the preparation of an ulttrathin film composed of non-flexible (rigid) functional molecules, wherein a non-flexible or rigid functional molecule can be defined as a functional molecule incapable of flexibly changing its conformations (special arirangements of atoms in the molecule) in compliance with the fixed electric charge of the surface onto which the molecule is to be adsorbed. For example, this method is not always useful in the preparation of an ultrathin film by layering functional molecules having a low molecular weight, since the method is based on the stabilization due to multi-site bondings. Although some cases are found in which the alternate layer-by-layer method is applied to certain types of dyes or bolaamphiphilic lipids, for stable layering such substances of a low molecular weight must be capable of associating with each other so as to behave in a manner similar to polymer ions.

Thus, the alternate layer-by-layer method cannot always be applied to a variety of low molecular-weight functional molecules. In addition, even when proteins are employed as functional molecules, particularly in layering enzymes such as glucoseoxidase, there may be a cases where no monolayer is formed because of the association of such molecules with each other in an aqueous solution. Improvement is therefore needed in the alternate layer-by-layer method to make it applicable to a wider range of functional molecules by eliminating the above-mentioned problems such as the association of the molecules.

SUMMARY OF THE INVENTION

The present invention is based on the discovery that the above-mentioned problems with respect to the alternate layer-by-layer method can be solved by mixing functional molecules with polymer ions beforehand (premixing) in a solution, and then carrying out alternate layering using the resultant solution.

The present invention thus provides a method for producing a functional thin film which comprises immersing a solid support having an electric charge in a (first) admixed polymer ion-functional molecule solution having a net electric charge opposite to that of the solid support followed by immersing the solid support in a (first) polymer ion solution having a net electric charge opposite to that of the (first) admixed polymer ion-functinal molecule solution, or alternatively immersing a solid support having an electric charge in a (second) polymer ion solution having a net electric charge opposite to that of the solid support followed by